Structural, thermal and mechanical properties of polymer nanocomposites based on organosoluble polyimide with naphthyl pendent group and layered double hydroxide

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Abstract
In this study, a soluble aromatic polyimide (PI) with naphthyl pendent group was initially synthesized by the reaction of pyromellitic dianhydride (PMDA) with 5-methyl-N,N-bis(4-nitrophenyl)naphthalen-1-amine. Then, via co-precipitation reaction of zinc nitrate hexahydrate and chromium nitrate nonahydrate, Zn/Cr-layered double hydroxide (LDH) was synthesized using hydrothermal techniques. Finally, different novel nanocomposites (NCs) based on PI and Zn/Cr-LDH (1, 2, 4 wt%) were produced through in situ polymerization. The resulting materials were characterized by Fourier transform infrared spectroscopy, X-ray powder diffraction, thermogravimetry analysis (TGA), field emission scanning electron microscopy, transmission electron microscopy, and mechanical testing. According to the TGA results, the prepared NCs showed high thermal stability at higher temperature due to the good dispersion and homogeneity of Zn/Cr-LDH in polymeric matrix. Consequently, the mechanical properties of the synthesized NCs were enhanced by the incorporation of 2 wt% Zn/Cr-LDH in the polymer matrix.

Keywords
Zn/Cr-layered double hydroxide, polyimides, in situ polymerization, thermal properties, tensile strength

Introduction
Polymer nanocomposites (NCs) are a class of hybrid materials composed of an organic polymer matrix with dispersed inorganic nanofillers. The integration of particulate fillers into the polymer matrices has been an extended method to improve the properties of neat polymers,¹² even though, from a reinforcing viewpoint, fibers, or at least fillers with laminate particles having a high shape factor, are more valuable reinforcing agents.³ In recent years, owing to the interesting results obtained by Toyota researchers concerning layered silicates as reinforcing fillers in polyamide and later for other thermoset and thermoplastic polymers, a big effort has been made to extend the study of new composites based on these nanolayered silicates.³ In many cases, addition of only a small amount of nano-clay to the polymer matrix is sufficient to make noticeable improvements in mechanical properties, thermal stability, heat distortion temperature, barrier performance, and flame retardance.⁵–¹² There are three main methods to prepare polymer–clay NCs, that is, solution methods, melt-processing methods, and in situ polymerization.¹³ Most of the published works have focused on organically modified smectite clays, in particular montmorillonites, as fillers of polymeric composites.¹⁴,¹⁵ Furthermore, the emphasis has recently been placed on layered double hydroxide (LDH) systems rather than clays due to the artificial preparation and highly tunable properties.¹³ LDHs, which frequently occur as hydrotalcite-like clays, are a kind of anion clays with unique properties that are not commonly observed in layered silicates.¹⁶ LDHs, that have also been known with two-dimensional lamellar...
structures for more than 150 years, are among the most studied advanced functional materials and have widely been applied in the fields of materials science, catalysis, environment protection, biology, and energy in recent years.\textsuperscript{17–20} The general formula for the LDH structure can be represented as: $(M^{2+}_{1-x}M^{3+}_{x}xH_2O)^{2+}(A^{m-}/x/nH_2O)^{m-}$, where $M^{2+}$, $M^{3+}$, and $A^{m-}$ commonly represent $Mg^{2+}$, $Al^{3+}$, and $CO_3^{2-}$ respectively.\textsuperscript{13,17} Their novelty originates from their broad range of chemical compositions, highly tunable properties, ease of synthetic procedures in the laboratory, stability in the air, interchangeable anions, and their potential industrial uses.\textsuperscript{21,22} Due to these advantages, different polymer/LDH NCs were synthesized and these NC materials have been evaluated for their potential applications in different areas.\textsuperscript{13}

Aromatic polyimides (PIs), as high-performance materials, have specific criteria including outstanding thermal resistance, mechanical strength, low specific density, superior flame resistance, and high conductivity and electrical and sound insulation properties.\textsuperscript{23–26} In spite of their excellent properties, PIs are difficult to fabricate due to their high glass-transition temperature and insolubility in most organic solvents. These properties make them generally intractable or difficult to process, thus limiting their applications.\textsuperscript{27} Thus, incorporating new functionalities to make PIs more tractable without deteriorating their own excellent properties has turned into one of the important goals of PIs chemistry.\textsuperscript{28,29} It has generally been recognized that the flexible linkages or bulky lateral groups, comparing with polymers without these linkages, impart better solubility and melt-processing characteristics as they cause separation of chains and lower chain packing with a free volume gain.\textsuperscript{24,25,28–31} As a result of these exceptional properties, aromatic PIs are expectant matrix candidates for hybrid materials as they show remarkable advances by introducing only a small fraction of inorganic additives.\textsuperscript{32–38}

In the preparation of the polymer/clay NCs, both the dispersion of nanofillers in the polymer matrix and the interaction between fillers and polymers are closely related to the properties of composites. Delozier and Dubois examined several approaches concerning the dispersion of clay into the PI matrices.\textsuperscript{39} Findings of this study showed that the best results were obtained by in situ polymerization techniques wherein polyamic acid (PAA) was synthesized in the presence of the clay. In this regard, herein, we wish to report a straightforward and simple method for preparing PI/LDH hybrids using in situ polymerization technique. To do so, Zn/Cr-LDH was initially synthesized by co-precipitation reaction of zinc nitrate hexahydrate $(Zn(NO_3)_2\cdot6H_2O)$ and chromium nitrate nonahydrate $(Cr(NO_3)_3\cdot9H_2O)$ by hydrothermal techniques. Then, a soluble aromatic PI containing pendant naphthyl groups was synthesized by the reaction of pyromellitic dihydride (PMDA) with 5-methyl-$N,N$-bis(4-nitrophenoxy)naphthalen-1-amine. Next, different organic–inorganic NCs of PI and Zn/Cr-LDH (1, 2, 4 wt%) were produced using in situ polymerization under the thermal imidization method. Morphological, mechanical, and thermal properties of the novel hybrid materials were evaluated by different techniques.

**Experimental phase of the study**

**Materials**

All materials and solvents were purchased from Merck Chemical Co. (Germany) and Aldrich Chemical Co. (St Louis, Missouri, USA) $Zn(NO_3)_2\cdot6H_2O$, $Cr(NO_3)_3\cdot9H_2O$, sodium hydroxide (NaOH), sodium carbonate (Na$_2$CO$_3$), 5-methylnaphthalen-1-amine, 1-fluoro-4-nitrobenzene, PMDA, palladium on activated carbon (10 wt%), and hydrazine hydrates were used as received. N-methyl-2-pyrroliodine (NMP), $N,N$-dimethylformamide, and $N,N'$-dimethylacetamide were dried over barium oxide, followed by fractional distillation. Deionized water was used throughout the experiments.

**Synthesis of Zn/Cr-LDH**

Co-precipitation method was used for the synthesis of the Zn/Cr-LDHs. First, a mixture of $Zn(NO_3)_2\cdot6H_2O$ and $Cr(NO_3)_3\cdot9H_2O$ and Zn: Cr in the molar ratio of 2.0:1.0 was dissolved in certain volume of deionized water. Then, the above solution and a mixture containing NaOH (2 M) and Na$_2$CO$_3$ (0.5 M) were simultaneously added to a three-necked flask at a speed of 1 drop s$^{-1}$. The pH of resulting suspension was maintained at 9–10 by continuous addition of 1 M NaOH. The mixed solution was stirred for 12 h and was then sonicated for 1 h. Finally, the mixture was transferred to Teflon-lined stainless steel autoclaves and the hydrothermal temperature was kept at 160°C for another 24 h. The resulting solid product was separated by centrifugation, washed with deionized water several times until pH = 7 and dried in an oven at 80°C for 6 h. This solid was labeled as Zn/Cr-LDH.

**Synthesis of diamine monomer**

5-Methyl-$N,N$-bis(4-nitrophenoxy)naphthalen-1-amine was synthesized according to the authors’ prior work:\textsuperscript{40} 6.30 mmol of 5-methylnaphthalen-1-amine, 12.60 mmol of 4-fluoronitrobenzene, 19 mmol of cesium fluoride, and 15 mL of dimethylsulfoxide (DMSO) were placed into a 50 mL three-neck-round-bottom flask. The mixture was heated while stirring at 110°C for 8 h under nitrogen atmosphere. The reaction mixture was cooled and then poured into 250 mL of ethanol to form a creamy precipitate of dinitro with naphthalen side group. The product was purified by recrystallization from glacial acetic acid to give 90% yield; melting point (m.p.) = 208–2210°C. Then, the dinitro was converted to diamine monomer using a...
catalytic amount of 10% palladium on activated carbon (Pd/C, 0.03 g) and 3 mL of hydrazine monohydrate in refluxing ethanol for 28 h to provide 78% yield; m.p. = 175–177°C.

Fourier transform infrared (FTIR; potassium bromide (KBr), cm⁻¹): 3455 (s), 3388 (s), 3117 (w), 3090 (w), 2920 (w), 1576 (m), 1555 (m) 1449 (w), 1366 (w), 1169 (w), 833 (m), 765 (w).

Proton nuclear magnetic resonance (¹H NMR; 500 MHz, DMSO-d₆, ppm): 3.03 (s, 3 H, CH), 4.64 (s, 4 H, NH), 6.67 (d, 8 H, Ar-H, J = 4.5 Hz), 6.96 (d, 1 H, Ar-H, J = 6.2 Hz), 7.37 (d, 1 H, Ar-H, J = 7.1 Hz), 7.69 (dd, 2 H, Ar-H, J₁ = 4.2 Hz and J₂ = 5.4 Hz), 7.77 (d, 1 H, Ar-H, J = 4.0 Hz), 7.88 (d, 1 H, Ar-H, J = 4.2 Hz).

**Preparation of PAA and pristine PI**

First, 2.037 g (0.006 mol) of the diamine monomer was dissolved in NMP (20 wt%) and cooled in an ice-water bath. Subsequent to being completely dissolved, 1.31 g of the PMDA (0.006 mol) was added into the above solution while stirring with a mechanical stirrer for 6 h at room temperature to obtain the pristine PAA. The PAA was converted into PI with a thermal imidization method. In this method, about 1.00 g of the PAA solution was placed into an oven at 80°C overnight (ca. 12 h) to remove the casting solvent. The semidried PAA film was further dried and converted into the PI by heating at 150 and 200°C, each for 1 h. To ensure imidization is completed, the PI films were further heated at 300°C for another 3 h.

**Preparation of PI/LDH NCs**

Various contents of Zn/Cr-LDH (1, 2, and 4 wt%) were dispersed in NMP (5 mL) under sonication for 2 h in order to prepare various concentrations of Zn/Cr-LDH nanoparticles. Diamine (0.51 g, 1.5 mmol) was added to flasks containing various concentrations of the LDH in NMP solution under a nitrogen purge in a sonic bath. After diamine was completely dissolved in the LDH/NMP solutions, 0.33 g under a nitrogen purge in a sonic bath. After diamine was completely dissolved in the LDH/NMP solutions, 0.33 g of PMDA (0.006 mol) was added and then the mixtures were stirred at room temperature under a nitrogen purge. The solid concentration of the solutions was kept at 10 wt% for all of the compositions. After 12 h, viscous PAA/LDH solutions were obtained. These PAA precursor solutions were cast into clean and dry glass substrates. The as-cast films were soft-baked at 80°C for 12 h and then thermally imidized using a stepwise imidization process under a nitrogen atmosphere for 1 h at 150°C and 200°C, and 3 h at 300°C.

**Results and discussion**

**Characterization techniques**

FTIR study. A diamine monomer containing naphthyl pendant groups (1b) was synthesized using a two-step process according to the synthesis pathway shown in Figure 1. The chemical structure of the synthesized diamine was proved by elemental analyses, FTIR, ¹H NMR, and ¹³C NMR spectroscopy techniques as reported in our recently published paper.³⁰ The formation of amine group for diamine monomer was confirmed by FTIR as was shown in the characteristic absorptions band in the region of 3448–3377 cm⁻¹ as well as by ¹H NMR as a peak at 4.61–4.63 ppm.

A soluble aromatic PI with naphthyl pendant group was synthesized by condensation of aromatic diamine and aromatic dihydride (PMDA) in a dry NMP using two-step condensation polymerization method, that is, the formation
of PAA followed by a thermal imidization of this compound to PI as shown in Figure 1.

Figure 2 shows the FTIR spectra of the PAA and PI. The characteristic of broad absorption at 3430–3190 cm\(^{-1}\) due to the amino (N–H) and hydroxyl (OH) groups, and amide carbonyl absorption at 1676 cm\(^{-1}\) were observed for PAA (Figure 2(a)). The FTIR spectrum of PI showed distinct features that clearly indicated the formation of imide ring and disappearance of the PAA peak during the thermal cyclization step. In the spectra of the PI, absorption bands of the imide groups appeared at 1774 and 1718 cm\(^{-1}\) for the antisymmetric and symmetric stretching vibrations of the carbonyl groups.\(^\text{41}\) The bands around 1374 and 816 cm\(^{-1}\) were ascribed to the stretching and bending vibrations of C–N–C in the imide ring (Figure 2(b)).

Figure 3 shows the FTIR spectra of the Zn/Cr-LDH and NCs of PI with 2 and 4 wt\% of LDH. LDH containing CO\(_3^{2-}\) anions had characteristic bands for various modes of infrared-sensitive vibrations of the anion.\(^\text{8,10,41}\) In this spectrum (Figure 3(a)), the broad absorption band in the region of 3100–3600 cm\(^{-1}\) was assigned to the OH stretching vibrations, \(\nu(\text{OH})\), associated with the basal hydroxyl groups and interlayer water. The bending vibration of the interlayer H\(_2\)O was also reflected in the broad bands around 1620 cm\(^{-1}\). The O–C–O asymmetric stretching vibration appears between 1363 cm\(^{-1}\) and 1507 cm\(^{-1}\). The bands at lower wave numbers such as 792, 552, and 431 cm\(^{-1}\) can
be assigned to the metal–oxygen stretching modes (Zn–O, Cr–O). Figure 3(b) and (c) shows the FTIR spectra of the PI NCs with different amount of Zn/Cr-LDH. In these spectra, the antisymmetric and symmetric stretching vibrations of the carbonyl groups of the imide, shifted from 1774 cm\(^{-1}\) and 1718 cm\(^{-1}\) to 1770 cm\(^{-1}\) and 1715 cm\(^{-1}\), respectively, in comparison to the neat PI. Moreover, in addition to the PI peaks, the FTIR spectra of the PI/LDH NCs showed new absorption bands at 700–400 cm\(^{-1}\) for metal-hydroxide sheets.\(^{41}\) This result confirmed that LDH was formed in the hybrid PI NCs.

**X-ray diffraction.** The XRD patterns of the synthesized Zn/Cr-LDH, pristine PI, and PI NCs with 2 and 4 wt% of Zn/Cr-LDH are shown in Figure 4. In the XRD patterns of Zn/Cr-LDH sample, the sharp and symmetric reflections were observed for (0 0 3), (0 0 6), (1 1 0), and (1 1 3) planes and broad asymmetric peaks for (0 0 9), (0 1 5), and (0 1 8) planes were observed and confirmed the characteristic planes of HT-like materials with hexagonal crystal system assuming a 3 R packing of layers.\(^{41,42}\) For ZnCr–CO\(_3\)\(^{2-}\)-LDH, the interlayer \(d\) spacing of characteristic (003) planes (\(d_{003}\)) at 2\(\theta = 11.26^\circ\) was found to be 0.78 nm which was similar to the values reported previously,\(^{41,42}\) indicating that Zn/Cr-LDH was well crystallized (Figure 4(a)). The XRD analysis for the pure PI exhibited a typical amorphous structure, which was associated with the broad peak of 2\(\theta\) at 15\(^\circ\) in the range from 10\(^\circ\) to 20\(^\circ\) (Figure 4(b)). XRD curves of the PI/LDH NCs are shown in Figure 3(c) and (d). No peaks in the range 2\(\theta = 1.2–10^\circ\) appeared when the Zn/Al-LDH contents were 2 and 4 wt%. This complete disappearance of LDH peaks may be due to the partial exfoliated structure, in which the gallery height of intercalated layers was large enough and the layer correlation was not detected by XRD. According to previous research, usually, there have been two types of NCs depending upon the dispersion of clay particles.\(^{8,10,41–43}\) The first type is an intercalated polymer/clay NCs, which consists of well-ordered multilayers of polymer. In these samples, the extent of polymer penetration is not sufficient to delaminate the ordered structures. The second type is an exfoliated polymer/clay NCs, in which there is a loss of ordered structure due to the extensive penetration of polymer into the silicate layers.

**FE-SEM study.** The FE-SEM images and EDS patterns of the Zn/Cr-LDH are shown in Figure 5. In general, LDH crystal has plate-like morphology and hexagonal crystallite. It was found that this sample showed the characteristics of plate-like morphology as well as spherical shape. The particle size distribution indicated that the size of LDH nanoparticles mainly ranged from 30 nm to 50 nm. In the FE-SEM images of the NCs with 2 and 4 wt% of Zn/Cr-LDH using two different magnifications, the plate like and spherical shape structures of LDH were observed (Figure 6(a) and (b)). Apparently, it seems that the particles were dispersed in the polymer matrix. In the NC with high-LDH concentration (NC4%), some aggregation may be observed in the FE-SEM images (Figure 6(c) and (d)).

**TEM study.** Figure 7 shows the TEM images of the Zn/Cr-LDH and PI NC with 2 of Zn/Cr-LDH using different magnifications. TEM images presented an actual image of nanoclay platelets to allow the internal morphology of nano-hybrids to be recognized. According to the TEM images, Zn/Cr-LDH had smooth overlapping crystals, and they were approximately in hexagonal form with uniform thickness which was commonly observed for typical LDH compounds (Figure 7(b) and (d)). For PI NC with 2 wt% of Zn/Cr-LDH, the particles seemed to be loose and not agglomerated were observed in the sample prepared by in situ polymerization, suggesting that this method may be suitable for dispersion of the inorganic filler in the polymer matrix (Figure 7(c) and (d)). The average particle size of the nanoparticles was in the range of 7–15 nm.
**Thermal properties**

Figure 8 shows the thermal degradation behavior of the PI/LDH hybrid films and neat PI film under nitrogen atmosphere. The temperature of 5% and 10% weight loss as well as char yield at 800°C were obtained from the thermograms and used as the criteria for the evaluation of thermal stability of the polymer NCs. The results of the TGA for neat PI and PI/LDH hybrid films with different weight percentages of Zn/Cr-LDH are shown in Table 1. Based on the results, it can be seen that the addition of Zn/Cr-LDH significantly increases the 5% and 10% weight loss temperatures. The initial decomposition temperature of the neat PI was about 378°C while it was higher for the NCs. This can be explained by high heat resistance exerted by the Zn/Cr-LDH nanoparticles. In reality, the presence of the hydrotalcite-like lamellae produces a barrier to oxygen diffusion into the heated polymer due to the accumulation of the oxides produced by thermal degradation of the material on the surface of the volatilizing polymer. This behavior indicates that LDH has great potential for polymer reinforcement. This material acts as thermal barrier heat sink and protects the polymer to be decomposed at normal temperature.

**Flame retardancy**

The non-flammability of neat PI and PI/LDH NCs was explained in terms of the value of limiting oxygen index.

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**Figure 6.** FE-SEM images of NCs with (a and b) 2% and (c and d) 4% of LDH. FE-SEM: field emission-scanning electron microscopy; NC: nanocomposite; LDH: layered double hydroxide.

**Figure 7.** TEM images of (a and b) Zn/Cr-LDH and (c and d) NCs with 2% of Zn/Cr-LDH. TEM: transmission electron microscopy; NC: nanocomposite.

**Figure 8.** TGA thermograms of (a) neat PI, and NC with (b) 1 wt%, (c) 2 wt%, and (d) 4 wt% of Zn/Cr-LDH. TGA: thermogravimetry analysis; PI: polyimide; NC: nanocomposite.

**Table 1.** Thermal characterizations of the pure PI and different PI/LDH hybrid films.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Material</th>
<th>$T_{5%}$ (°C)$^a$</th>
<th>$T_{10%}$ (°C)$^a$</th>
<th>Char yield (%)$^b$</th>
<th>LOI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure PI</td>
<td>410</td>
<td>418</td>
<td>68</td>
<td>44.7</td>
</tr>
<tr>
<td>2</td>
<td>PI/LDH NC1%</td>
<td>430</td>
<td>468</td>
<td>70</td>
<td>45.5</td>
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<tr>
<td>3</td>
<td>PI/LDH NC2%</td>
<td>438</td>
<td>493</td>
<td>73</td>
<td>46.7</td>
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<tr>
<td>4</td>
<td>PI/LDH NC4%</td>
<td>447</td>
<td>508</td>
<td>74</td>
<td>47.1</td>
</tr>
</tbody>
</table>

PI: polyimide; LDH: layered double hydroxide; NC: nanocomposite; TGA: thermogravimetry analysis; $T_S$: temperature at 5% weight loss; $T_{10\%}$ temperature at 10% weight loss.

$^a$ $T_S$ and $T_{10\%}$ were recorded by TGA at a heating rate of 20°C min$^{-1}$ under a nitrogen atmosphere.

$^b$ Percentage weight of material left undecomposed after TGA analysis at maximum temperature 800°C under a nitrogen atmosphere.
LOI. The LOI values were calculated from the char yield obtained from TGA analysis using Van Krevelan and Hofytzr equation as shown below:

$$\text{LOI} = 17.5 + 0.4 \text{CY},$$

where LOI is the limiting oxygen index and CY is char yield. As the Zn/Cr-LDH content was increased in the NCs, char yields were also increased from 70% to 74%. This indicated that the incorporation of Zn/Cr-LDH in the PI enhanced the char yield. The LOI values of the NCs were in the range of 45.5–47.1%, which was above the threshold value of 44.7% (Table 1). It showed that all the PI/LDH NCs could be classified as self-extinguishing and flame-retardant materials.

**Mechanical properties**

The tensile properties of the PI/LDH NC films were examined using tensile testing in terms of the increased degree of tensile strength relative to the pure PI as function of Zn/Cr-LDH content; their stress–strain curves are shown in Figure 9. It was clearly seen that, compared to PI, the properties of PI/LDH improved. When the weight content of the reactive HNTs was 2%, the tensile strength of NC2% could be up to 137.4 MPa and increased by 25.7% compared with pristine PI (109.3 MPa). The good dispersion of the Zn/Cr-LDH in the polymer matrix could decrease the stress concentration and afford even more stress distribution. Besides, the better compatibility and interfacial interaction between polar hydroxyl groups of LDH and polymer matrix could further improve the mechanical properties of the PI/LDH NC films. Further additions of LDH (4 wt%) did not enhance the strength because of increasing brittleness, as little amount of Zn/Cr-LDH was aggregated to form a defect in the NCs, thereby reducing tensile strength. The elongation at break of PI/LDH NC increased compared to PI. PI/LDH NC2% had the maximum elongation at break, up to 15.8%. The reason was that the interfacial adhesion between polymer matrix and Zn/Cr-LDH was strong enough to improve the plasticity of the polymers. However, the elongation at break of PI/LDH NC4% was decreased (Figure 9). It was concluded that the low content of the Zn/Cr-LDH had good dispersion on the polymer matrix and when the content Zn/Cr-LDH was high, more particles aggregated and the interfacial defects occurred, resulting in the reduction of the interfacial adhesion.

**Conclusions**

In this study, novel PI/LDH NCs were successfully prepared by in situ polymerization technique. The influences of Zn/Cr-LDH loading on the morphological, thermal, and mechanical behavior of PI/LDH NCs were successfully investigated. TEM and XRD results showed that the Zn/Cr-LDH nanoparticles were mostly dispersed throughout the polymer matrix and the layers were disorderly oriented, providing an ample evidence of crystal layer delamination/exfoliation from the surfaces. Dispersed LDH platelets in the PI matrix were found to increase the thermal stability including thermal decomposition temperature and char yield of PI/LDH NCs. The increase of the thermostability at high-degradation stages was due to the hindering effect of LDH layers which could trap the volatile gases. The tensile strength increased with growing amount of Zn/Cr-LDH up to certain content (2 wt%). For the PI/LDH NCs, the maximum degree of tensile strength was observed at a LDH of 2 wt%, corresponding to an almost 25% increase in tensile strength compared to pure polymer.

**Declaration of Conflicting Interests**

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**References**


